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H. Ti Tien, Principal Investigator

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The main objective will be to understand the mechanism of charge generation, separation and transport in electron-conducting bilayer lipid membranes in which one side of the membrane is a cathode and the other is an anode. Our approach may be thought of as a unique way to investigate the diode effect of a molecular junction free from the usual bulk solid effects. Currently available conducting polymers and a variety of novel compounds to be synthesized will be incorporated into these ultrathin lipid films for study. The electrical and photoelectrical properties of these ultrathin films separating two aqueous solutions will be investigated by but not limited to, photoelectrospectrometry and cyclic voltammetry recently developed and applied by our laboratory to membrane and ultrathin film research.

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PROGRESS REPORT ON CONTRACT N00014-85-K-0399

PRINCIPAL INVESTIGATOR: H. Ti Tien

CONTRACTOR: Michigan State University

CONTRACT TITLE: Electrochemistry of Bilayer Lipid Membranes

DATE: 16 June 1988

RESEARCH OBJECTIVE: The objective of this project is to obtain an understanding of the principles at the molecular level governing the molecular junction effect in electron-conducting ultrathin bilayer lipid membranes (BLM). Specifically, it is proposed to:

- 1) investigate the nature and mechanisms of charge carrier generation, transport, redox reactions and energy transduction pertinent to membrane bioenergetics,
- 2) reconstitute specific biomembrane systems with lipid bilayers and their modification so that simple physical, chemical and physiological processes may be isolated and analyzed in terms of their constituents,
- 3) use pigmented BLMs to obtain information on light-induced molecular events, and
- 4) construct biosensors and energy transducers using modified ultrathin lipid membranes.

PROGRESS: As evidenced by the list of publications, we have made progress in the last 12 months. Specifically,

- 1) The conduction properties of lecithin bilayer membranes in iodine-containing solutions were examined from a potentiodynamic experimental approach. Voltammetric data obtained by using a variety of forms (derived from charge-transfer type interactions) of iodide implicate the triiodide ion as the charge carrier accounting for the diffusion-limited voltammetric response whereas the charge transport of iodide seems to be limited by transmembrane diffusion. The data were used to support one of the many proposed mechanisms for conductance of iodide in membranes.

Dynamically obtained current/voltage curves of bilayer lipid membranes partitioning a solution of lipophilic ions have been compared with the results of the type expected in a voltammetry experiment involving ionic transport across a liquid/liquid interface. Lipophilic ions yielding "voltammograms" analogous to reversible and irreversible voltammograms (in conventional electrochemical systems) have been found. Examples of ions were found which yield what may be analogous to a masked response, a phenomenon known in the literature of liquid/liquid interfaces. Although the behavior of the two systems is similar, there exist differences in the interpretation of the

voltammograms and suggestions were offered for an energetic and mechanistic interpretation of the membrane voltammogram.

- 2) The phenomenon of inorganic substances deposited onto the bilayer lipid membrane was investigated. Metallic copper and semiconducting compounds such as CuS, FeS, CdS and also AgBr were deposited onto the bilayer lipid membrane. The cyclic voltammetry technique was used for determining electrochemical and photoelectrical properties of coated membranes. Considerable increase of stability and drastic changes of membrane properties were observed. Also investigated were the photoelectrical properties of bilayer lipid membrane with dispersed CdSe or AgBr particles in the absence and presence of pigments.
- 3) The ionic permeability coefficients, ionic transference number, activation energy of ion transport and breakdown voltage of bilayer lipid membranes made from dioleoylphosphatidylcholine or its mixtures with dolichyl 12-phosphate have been studied. The electrical measurements showed that dolichyl phosphate in phospholipid bilayers decreases membrane permeability, changes membrane ionic selectivity and increases membrane stability. These results were examined in light of the aggregation behavior and the intramolecular clustering of a dolichyl phosphate molecule in phospholipid membranes. From our data we have suggested that the hydrophilic part of dolichyl phosphate molecules regulates their behavior in membranes, and
- 4) A new type of bilayer lipid membrane (BLM) was reported with aqueous interfaces which are formed from thermotropic liquid crystals (nematic-6CB, smectic-8CB, and cholesteric-cholesteryl palmitate, ChP). The electrical properties of these unmodified membranes have been investigated. We suggest that BLMs of this type in their 'black' states consist of two molecular layers with a smectic-like structure.

The light-induced capacitance changes and both photovoltage and photocurrent generated by pigmented liquid crystal bilayer (PBLM) with a fixed surface asymmetry were measured under continuous illumination. It was suggested that the origin of the photoresponses is due to electron injection across the two double layers resulting from the interaction of an excited photosensitizer located in the BLM with the acceptor ions in the solution. The photocurrent across the double layers affects their properties (potential across those layers, a dielectric constant and a concentration of acceptor ions around the double layers) which can be seen in the PBLM capacitance changes.

The light-induced capacitance changes and also both photovoltage and photocurrent under continuous illumination have been investigated in pigmented liquid crystal bilayer membranes (PBLM) containing TCNQ as photosensitizer with Na₂SO₃ electron donor on one side and methylene blue electron acceptor on the other side. The results have shown that TCNQ in cyanobiphenyl membrane produces a unique photoactive BLM system in which all three main parameters (conductivity, capacity and voltage across the membrane) are in a wide range altered by the light. It has been shown that a TCNQ-cyanobiphenyl charge transfer complex is responsible for the observed photochanges. The possible mechanism of photoinduced electrical effects in this type of PBLM has been examined.

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WORK PLAN: In the coming months we plan to continue experiments on BLMs formed from liquid crystals, interaction of drugs with reconstituted membranes, and BLM-based electrochemical/bio sensor development. In particular, experiments are under way to measure electrical parameters of BLMs in terms of specific ligand-receptor interactions, according to our original proposal. Due to complexities of the biomembrane structure and environmental factors associated with it, planar BLMs will be used in the elucidation of membrane processes using a number of electrical methods developed in our laboratory.

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